UNIVERSITI PUTRA MALAYSIA

ELECTROCHEMICAL STUDIES OF C_{60}-FULLERENE MICROCRYSTALS ATTACHED TO A SOLID STATE ELECTRODE

LIM EI BEE

FSAS 2002 3

ELECTROCHEMICAL STUDIES OF C_{60}-FULLERENE MICROCRYSTALS ATTACHED TO A SOLID STATE ELECTRODE

By

LIM EI BEE

Thesis Submitted to the School of Graduate Studies, University Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

March 2002

Dedicated to my parents, my brothers Leng, Hall, Teong and Hao, my friends Chew, Sim and Lee, for their support, patience and friendship

Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in the fulfilment of the requirement for the degree of Master of Science

ELECTROCHEMICAL STUDIES OF C_{60}-FULLERENE MICROCRYSTALS ATTACHED TO A SOLID STATE ELECTRODE

By

LIM EI BEE

December 2001

Chairman: Associate Professor Tan Wee Tee, Ph.D.

Faculty: Science and Environmental Studies

Electrochemistry behaviours of C_{60} attached with physical method: solvent casting and mechanically attachment, to various solid-state electrode surfaces (gold, glassy carbon and platinum) were studied in aqueous and non-aqueous solution containing a variety of doping cations such as Group I alkali-metal cations and quaternary-ammonium R_4N^+. Electroreduction and reoxidation of microcrystalline C_{60} in 0.1 M $TBAPF_6$/ACN showed one to four pairs, characteristic solid state current-potential curve, with only first and second pairs appeared to be stable and reversible.

In contact with 0.1 M $TBAPF_6$/ACN, the large peak separation and small maximum at reverse scan observed with cyclic voltammetric experiments, as well as the current-time transients obtained in chronoamperometric experiments produce evidence of nucleation and growth (N&G) processes at the electrolyte-solid-electrode interface.

C_{60} cast onto glassy carbon or gold electrodes showed very different results of cyclic voltammetry (CV), chronocoulometry (CC), and chronoamperometry (CA) in aqueous and non-aqueous solutions. With the presence of alkali-metal cations in aqueous electrolyte, M_nC_{60} ($M = Li^+, Na^+, K^+, Rb^+, Cs^+$, n = 1 to 6) was formed at the end of potential scan, and the loss of faradaic activity when oxidizing M_nC_{60} at reverse of potential scan indicated the formation of non-electroactive and irreversible species. In aqueous solution, CV results showed a parallel shift in reduction peak position as the sizes of cation increased.

A glassy carbon electrode modified by C_{60} coat was used to mediate the oxidation of cysteine in contact with an aqueous electrolyte containing potassium cation. Under conditions of cyclic voltammetry, the potential of cysteine is lowered by approximate 100 mV and current is enhanced significantly relative to the situation prevailing when a bare glassy carbon electrode is used. Mediation also occurs when the potential range covered include that of C_{60}/C_{60}^{n-} redox couples.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENGAJIAN ELEKTROKIMIA BAGI C_{60}-FULLERIN MIKROKRYSTAL YANG TERLEKAT PADA SESUATU ELEKTROD PEPEJAL

Oleh

LIM EI BEE

Disember 2001

Pengerusi: Profesor Madya Tan Wee Tee, Ph.D.

Fakulti: Sains dan Pengajian Alam Sekitar

Tingkahlaku elektrokimia bagi C_{60} yang dilekatkan secara fizikal melalui "kot larutan" dan "lekatan mekanikal", kepada permukaan pelbagai elektrod pepejal (emas, karbon kaca dan platinum) telah dikaji dalam larutan akues dan tak akues yang mengandungi pelbagai kation berdop seperti kation logam-alkali Kumpulan I dan kuaternari-ammonium R_4N^+. Elektro-penurunan dan pengoksidaan bagi mikrokristal C_{60} dalam 0.1 M $TBAPF_6$/ACN menunjukkan satu hingga empat pasang kelok arus-keupayaan yang berperanan pepejal, dengan hanya pasangan pertama dan kedua berkelakuan stabil serta boleh berulang.

Berhubungan dengan 0.1 M $TBAPF_6$/ACN, pemisahan besar antara puncak dan maksima kecil pada imbasan terbalik yang diperhatikan dengan eksperimen voltammetri berkitar, serta transian arus-masa yang diperolehi dalam eksperimen kronoamperometri menghasilkan bukti bagi proses penukleusan dan tumbesaran (N&G) pada antara-fasa elektrolit-pepejal-elektrod.

C_{60} yang disapu ke atas elektrod karbon kaca atau emas menunjukkan keputusan voltammetri berkitar (CV), kronokulometri (CC), dan kronoamperometri (CA)

dalam larutan akues dan tak akues yang amat berbeza. Dengan kehadiran kation logam-alkali dalam elektrolit akues, M_nC_{60} ($M = Li^+, Na^+, K^+, Rb^+, Cs^+$, $n = 1$ to 6) telah dihasilkan pada akhir imbasan keupayaan, dan juga, kehilangan aktiviti faradaik semasa pengoksidaan M_nC_{60} pada imbasan keupayaan terbalik menandakan pembentukan sesuatu spesies yang tidak eletroaktif dan tidak berulang. Dalam larutan akues, keputusan CV menunjukkan satu anjakan selari pada kedudukan puncak penurunan dengan saiz kation yang meningkat.

Satu elektrod karbon kaca yang diubahsuiakan dengan kot C_{60} telah digunakan untuk memediankan pengoksidaan sistena dalam suatu elektrolit akues yang mengandungi kation potassium. Di bawah kawalan voltammetri berkitar, keupayaan sistena telah diturunkan lebih kurang 100 mV dan arusnya jelas ditingkatkan berbanding dengan situasi biasa iaitu bila sesuatu elektrod karbon kaca tanpa ubahsuian digunakan. Pemedianan juga berlaku bila julat keupayaan yang dilingkungi termasuk pasangan redoks C_{60}/C_{60}^{n-}.

ACKNOWLEDGEMENTS

My supervisor, Assoc. Prof. Dr. Tan Wee Tee certainly is the first and most important person whom I would like to acknowledge. Thank you for your guidance, help, suggestion and patience throughout the duration of this project. My sincere appreciation also goes to my co-supervisor Assoc. Prof. Dr. Zulkarnain Zainal and Assoc. Prof. Dr. Anuar Kassim for their for their valuable time, effort and support during my study.

Along the way, I have been assisted by my course-mates and friends who share their knowledge with me. I would particularly like to thank Ng Geok Khoon, Chew Won Yin, Sim Leng Tze, Lee Chiu Sze, and Lim Kean Pah. Finally yet importantly, I wish to convey my deepest gratitude to my family, my housemates, and all of my friend who help me a lot in one and another way in the preparation of this project.

I gratefully acknowledge the award of the PASCA scholarship from Universiti Putra Malaysia, which enable me to undertake this work.

I certify that an Examination Committee met on 11 February 2002 to conduct the final examination of Lim Ei Bee on her Master of Science thesis entitled "Electrochemical Studies of C_{60}-Fullerene Microcrystals Attached to a Solid State Electrode" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulation 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

MD JELAS HARON, Ph.D.
Associate Professor,
Faculty of Science and Environmental Studies
Universiti Putera Malaysia
(Chairman)

TAN WEE TEE, Ph.D.
Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

ANUAR KASSIM, Ph.D.
Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

ZULKARNAIN ZAINAL, Ph.D.
Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

SHAMSHER MOHAMMAD RAMADILI, Ph.D.
Professor/Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia.

Date: 8 APR 2002

The thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of the requirement for the degree of Master of Science.

AINI IDERIS, Ph.D.
Professor/Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 13 JUN 2002

DECLARATION

I hereby declare that this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

LIM EI BEE

Date: 23-03-2002

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES